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(54) HIGH MODULUS FILAMENTS

(71) We, ANIC S.p.A., an Italian company, of Via M. Stabile 216, Palermo, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of obtaining very high-modulus filaments, the method being simpler and more convenient than known methods. The method of this invention uses considerably simplified apparatus which is more practical to use.

There are known three methods which employ deformation in the solid phase to form filaments. The expressed "deformation in the solid phase" denotes a method in which a polymer is deformed below its melting point. The three methods which employ deformation in the solid phase are (1) drawing the solid polymer between rollers which rotate at different speeds, (2) extruding the solid polymer through a nozzle by means of a plunger sliding within a cylinder (ram extrusion), and (3) hydrostatic extrusion in which the solid polymer is forced through a nozzle by the application of hydrostatic pressure. By such prior methods, satisfactory orientation of the extruded polymer can be achieved, as is reflected in the satisfactory modulus of elasticity (i.e. Young's modulus, E) of the extrudate.

Optimum orientation features can be obtained by selecting a starting material having a high-draw-ratio. The draw-ratio of a polymer is the ratio of the maximum length obtained by drawing a polymer sample to its original length prior to drawing. High draw-ratios can be obtained by special heat treatments such as those described in British Patent No. 1,469,526. In these heat treatments, the melted polymer is cooled from a temperature higher than, or equal to, the melting point temperature of the polymer concerned, at a controlled speed of cooling. In one method, the melted polymer is cooled to the ambient temperature. In another method, the melted polymer is cooled to a temperature below the crystallisation temperature and is subjected to subsequent quick quenching from the crystallisation temperature. In a third method, the polymer is kept at a temperature below the melting point temperature, but in the vicinity of such temperature, for a certain time.

All of these methods result in high-modulus filaments. However, they suffer from severe limitations as regards the processing conditions (i.e. the necessity of accurate programming and intricate control of the temperature and the necessity of the use of high pressures) and the productive capacity (i.e. the low production speeds, of the order of magnitude of a few centimetres per minute).

According to the present invention, there is provided a method for the production of a drawn polymer filament, which method comprises (A) subjecting a filament of a polymer having a degree of crystallinity greater than 30% to deformation in the solid phase by drawing through a nozzle having (i) a diameter of from 0.15 to 0.90 times the diameter of the filament, (ii) a diameter not greater than 5 mm and (iii) an intake angle of less than 60°; and (B) cooling the drawn filament leaving the nozzle.

The present invention relates to a method for obtaining highly oriented filament, which consists in subjecting an orientable polymer to a novel solid phase deformation procedure. The invention also relates to a filament of high-density polyethylene having its dimensions more developed in one direction than in the other two directions, the smallest dimension being longer than 0.01 mm and the filament having a Young's modulus (E) higher than 3.0×10^{10} N/m².

This invention also relates to a filament of polyoxymethylene having a dimension more extended in one direction than in the other two directions, the smallest dimension being less than 0.01 mm and the Young's modulus being higher than 1.0×10^{10} N/m².

The invention can be applied to crystallisable polymers. Crystallisable polymers are polymers which form a crystalline (or para-crystalline) structure when a melt thereof is cooled or when the solvent of a solution thereof is evaporated.

Straight-chain polymers, i.e. polymers, i.e. polymers in which the molecules have a very small number of branch chains per molecule, are preferred.

Examples of suitable polymers are hydrocarbonaceous hydrocarbons such as polyethylene and polypropylene; oxygen-substituted hydrocarbonaceous polymers such as polyethylene oxide, polyoxymethylene and polyacetaldehyde; polyamides; linear polyesters; and fluorinated polymers such as polytetrafluoroethylene and polytrichlorofluoroethylene.

Copolymers of, for example, ethylene, polypropylene and polyoxymethylene can also be used, provided that the percentage of comonomer therein is not so high or so arranged alongside the chain as to hinder crystallisation.

The crystallisable polymer must have an adequately high molecular weight, the value of which depends upon the polymer concerned, and must have a sufficiently close distribution of the molecular weights. In the case of high-density polyethylene, the preferred weight average molecular weights, as measured by gel-permeation chromatography (GPC), are in the range of from 30,000 to 600,000, and the preferred distribution of molecular weights, expressed as the ratio of the weight average molecular weight to the arithmetic mean molecular weight, is from 2 to 10.

By the method of the present invention, there can be drawn, at a temperature below the melting point temperature, filaments having a circular cross-sectional shape or any other shape produced beforehand according to a procedure which imparts to the material of which the articles is made a degree of crystallisation higher than 30%. The term "degree of crystallization" (i.e. "crystallinity") means the fraction of polymer in the crystalline state, as measured by X-rays or by specific gravity measurements.

The term "draw" used herein means the drawing of a filament through a nozzle, slot or other orifice by means of a force applied to either end of the filament.

According to the method of this invention, the extruded filaments of a crystallisable polymer are preferably produced at a temperature which does not exceed by more than 70°C the melting point temperature. For high-density polyethylene, an extrusion temperature of 150°C is preferred whereas for polypropylene and polyoxymethylene, a temperature of 200°C is preferred.

The filaments are preferably drawn through a nozzle which has a conical inlet and which is very short, at a temperature below the melting point temperature. The angle of intake of the nozzle is preferably about 30°, and the nozzle preferably has a circular cross-section. The diameter of the nozzle is preferably from 0.15 to 0.80 times the diameter of the filament to be drawn, more preferably from 0.15 to 0.35 times such diameter. In addition, the diameter of the drawn filament should be considerably less than the diameter of the nozzle, in contrast to the hydrostatic exarusion method in which the diameter of the filament is greater than, or equal to, the diameter of the nozzle.

The temperature of draw depends upon the polymer which is used but is generally from the melting point temperature to a temperature which is 120°C below the melting point temperature.

The pulling force can be applied by any device which is capable of pulling the filament continuously.

A lubricant fluid is preferably introduced into the nozzle to reduce friction between the polymer and the nozzle. The preferred lubricant liquids are those which have a coefficient of friction between that of the polymer and that of the metal from which the nozzle is made.

It has been found that a quick cooling of the filament permits one to increase both the drawing speed and the draw-ratio, the likelihood of breakage of the filament thereby being reduced.

The preferred temperature to which the drawn filament is cooled is at least 20°C below the extrusion temperatures. Also, it is preferred that the filament be cooled as close to the nozzle as physically practicable. These measures are an essential part of the present invention.

In the method of this invention, no high pressures are required. The forces which are required for carrying out the pull or draw are modes (e.g. a few kilograms for

a filament having an initial diameter of from 1.2 to 1.3 mm). The speed of production can be about 40 m/hour, which is considerably above that obtainable with the prior methods, and very high drawing ratios, of the order of magnitude of from 20 to 30, can be achieved.

The filaments which are obtained usually have a high modulus and a low shrinkage when subjected to temperatures below the melting point temperature. When the drawing temperature is high, the filaments are transparent, have a high modulus E, and have a specific gravity heavier than that of the filament from which they are drawn.

In order to improve the properties of the filaments, it is possible to incorporate into the polymers, fillers of varied form such as fibrous form or spherical form or other form.

It is possible to improve the process of this invention by raising the draw speed to values of a few hundred metres per minute, provided that the maximum draw-ratio for the polymer concerned is not exceeded. In such cases, the draw-ratio can be about 10 and the modulus can be below 20 GPa.

The filaments obtained can be subjected to a further draw process which can be performed by a conventional draw method, such as by means of two rollers which rotate at different speeds. This second drawing step produces filaments which have, for example, a draw-ratio of the order of magnitude of 20 to 30, a very high modulus E, and a very low shrinkage.

For a better understanding of the invention, reference will now be made, by way of example, to the accompanying drawing in which:

Figure 1 is a schematic representation of the formation of an extrudate filament; and

Figure 2 is a schematic representation of the subsequent drawing of the extruded filament.

Referring to Figure 1, a polymer is extruded from an extruder 1 to form an extruded filament 2 which is wound onto a take-up drum 3. Referring to Figure 2, the extruded filament 2 of Figure 1 is drawn from a drum 1 through a heating tunnel 2 and through a nozzle at the bottom of the tunnel. The drawn filament leaving the nozzle is drawn into a bath 3 containing a coolant 4. The filament is then drawn over a guide roller 5 onto a take-up drum 6.

The apparatus shown in Figure 1 and 2 is shown schematically, since each individual part of the apparatus is conventional in itself.

The invention will now be illustrated by the following Examples. The Examples show that the polymer extrudate, when drawn, is subjected to a drag of from 5 to 500 kg/cm², preferably from 50 to 200 kg/cm². The stress relates to the surface area of the cross-section of the filament prior to drawing, i.e. a filament such as filament 2 in Figure 1.

EXAMPLE 1.

This Example describes the production of polyethylene filament having a high Young's modulus E.

High-density polyethylene of commercial make was used. The polyethylene had the following physical properties:

Density (specific gravity)	0.96
Weight average molecular weight	72,000
Arithmetical mean molecular weight	18,000
Young's modulus, E	1.3 GPa.

The polyethylene was extruded in air at 150°C so as to form a filament having a diameter of 1.3 mm. The density of the filament was 0.961 and its intrinsic draw-ratio was 12 at 23°C and 25 at 80°C. One end of the filament, after having been pulled with a dynamometer, was introduced into a nozzle having a diameter of 1 mm and a half-angle of intake of 15°, the nozzle temperature being 100°C. The filament end leaving the nozzle was fastened to a cylinder which was rotated at a surface speed of 8 m/hour. There was obtained a filament which has a diameter of 0.284 mm (corresponding to a draw-ratio of 21) and a Young's modulus E of 34 GPa (measured with a Rheovibron DDV II at a frequency of 110 hz at room temperature). The pulling force was weaker than 20N. The filament was opaque.

The above procedure was repeated at 110°C, while rotating the cylinder at a surface speed of 5 m/hour. The filament thus obtained has a diameter of 0.260 mm

(which corresponds to a draw-ratio of 25), a Young's modulus E of 40 GPa and a pulling force equal to that of the above filament. The filament was transparent and has a density of 0.969. At temperatures below 120°C the shrinkage of the fibre was less than 2%.

Upon comparison these results with those obtained by the hydrostatic extrusion method described above, it can be seen that the characteristics of the respective filaments obtained are similar as regards the modulus and transparency. In British Patent Specification No. 1,480,479, the maximum reported value for E is 46 GPa (obtained by a procedure different from that used herein). However, sharp quantitative and qualitative differences are observed as regards the speed of production, the forces and pressures which are necessary, and the ratio of the nozzle diameter to the diameter of the fibre produced. In order to achieve draw-ratios greater than 20 when drawing at 100°C, it is not possible to use speeds higher than 1 cm/minute in the case of the hydrostatic extrusion method, whereas in the case of the procedure of this Example, there is achieved a speed of 8 m/hour (corresponding to 13 cm/minute), a speed which is at least 13 times as much. In the case of the pressures and forces required in the method of this Example, a comparison cannot be made directly since two non-homogeneous physical magnitudes are concerned. However, compared to the high pressures (1,300 bars) used in the hydrastatic extrusion process of British Patent Specification No. 1,480,479 the pressures used in the method of this Example are small (20 N).

Moreover, the process of this Example differs qualitatively from the hydrostatic extrusion process since in the latter the diameter of the filament is equal to (at high draw-ratios) or higher than (at low draw-ratios) the nozzle diameter [Journal of Materials Science, *9*, 1193, (1974)].

EXAMPLE 2.

This Example describes the production of a filament having a very high Young's modulus E, at a high production speed.

Filaments were prepared by extrusion and were subjected to drawing as in Example 1. Beneath the nozzle, there was placed a bath which contained a liquid coolant so that the filament emerging from the nozzle passed into the coolant immediately upon leaving the nozzle and prior to being drawn.

The draw-ratio was from 22 to 25 when drawing at 100°C and when water was used as the coolant. The speed of production was at least four times greater than in Example 1. The other properties of the filament, namely modulus E, transparency and shrinkage, were the same as those of the filament produced according to Example 1.

EXAMPLE 3.

This Example describes the production of a filament having a very high Young's modulus E, at a high production speed according to the procedure set forth in Example 1.

Filaments were prepared by extrusion and were subjected to drawing as in Example 2. The nozzle was fed with an appropriate liquid lubricant, namely glycerol, a 1:1 glycerol-water mixture, ethanol, water, castor oil, "Molykote M 30 (made by Dow Corning Corporation), n-pentane or kerosene. It was found that the liquid lubricants increased the average speed of production by a factor of two relative to Example 2. The properties of the filaments were the same as those of Example 1.

EXAMPLE 4.

This Example describes the production of filaments having a high Young's modulus E, from polymers of ethylene and from a copolymer, according to the procedure already described in Example 1.

Commercial high-density polyethylenes (referred to as polymers A, B and C) and an experimental copolymer of ethylene and butadiene containing 3% by weight of butadiene were used. The results obtained are given in Table 1.

TABLE 1

Polymer	MFI (g/10 minute)	Density of filament	Maximum draw-ratio	Modulus E (GPa)
A	2.3	0.963	20	37
B	9.0	0.961	25	40
C	12	0.962	18	34
Experimental copolymer	2.1	0.947	17	20

The MFI index is a measure of the fluidity of the material in the molten condition. It was measured under standard conditions according to ASTM D—1238—7T using a load of 2.16 kg at 190°C.

The results tabulated in Table 1 show that the homopolymers of polyethylene are particularly interesting for the production of very high modulus fibres and that there is an MFI range in which high draw-ratios and high moduli can simultaneously be obtained. With the copolymers, comparatively high draw-ratios and moduli can be obtained, but they are less than the maxima obtainable with the homopolymers.

EXAMPLE 5

This Example relates to the production of filaments having a high modulus, from polymers of polyoxymethylene according to the procedure described in Example 1.

There were used two kinds of polyoxymethylene namely, Debrin 500 and Debrin 150 (made by E.I. DuPont de Nemours & Co.). The procedure described in Example 1 was used, except that the temperature of the nozzle was 160°C. The results tabulated in Table 2 were obtained.

TABLE 2

Polymer	MFI (g/10 minute)	Density	Draw-ratio	Modulus E (GPa)
DEBRIN–500	5	1.42	10	21
DEBRIN–150	1	1.42	10	20

The speed of extrusion was 5 m/hour (corresponding to 8.3 cm/minute) and the pulling force was less than 20 N. In comparison in the hydrostatic pressure method, the equivalent speed is 0.025 cm/minute (British Patent No. 1,480,479, Example 3).

EXAMPLE 6.

This Example describes the production of filaments having a high modulus, from polypropylene according to the procedure described in Example 1.

There was used a polymer which has weight average molecular weight of 170,000. The extrusion was carried out at 200°C, and drawing, carried out at a nozzle temperature of 130°C, gave a filament having a Young's modulus E of 17 GPa and a draw-ratio of 16.

EXAMPLE 7.

This Example describes the production of polyethylene filaments having a high Young's modulus E, by extrusion and subsequent drawing.

The polyethylene used was the same as that described in Example 1. Extrusion in air at 150°C of the polyethylene gave a filament having a diameter of 0.45 mm. The filament was then drawn at 100°C through a nozzle having a diameter of 0.30 mm, a length of 0.30 mm and an intake half-angle of 15°. Beneath the nozzle there was arranged a bath containing a liquid coolant as described in Example 2.

It was found that the filament could be taken up at a speed of a few hundred metres per minute. At that speed the diameter of the filaments was 0.20 mm, and the draw-ratio was 5.1.

The filaments were further drawn between two rollers one of which was rotated four times faster than the other. After being passed between the rollers, the filament was passed through a bath of water at 60°C, the bath length being 2 m. The resulting filament had a diameter of 0.10 mm (which corresponds to an overall draw-ratio of 20), a Young's modulus E of 32 GPa, and a shrinkage of less than 2% at temperatures under 120°C.

WHAT WE CLAIM IS:—

1. A method for the production of a drawn polymer filament, which method comprises (A) subjecting a filament of a polymer having a degree of crystallinity greater than 30% to deformation in the solid phase by drawing through a nozzle having (i) a diameter of from 0.15 to 0.90 times the diameter of the filament, (ii) a diameter not greater than 5 mm and (iii) an intake angle of less than 60°C; and (B) cooling the drawn filament leaving the nozzle.

2. A method according to claim 1, wherein the filament is drawn at a temperature of from the melting point of the polymer to a temperature 120°C below the melting point of the polymer.

3. A method according to claim 1 or 2, wherein the nozzle has a diameter of from 0.15 to 0.35 times the diameter of the filament.

4. A method according to any of claims 1 to 3, wherein the nozzle has an intake angle of about 30°C.

5. A method according to any of claims 1 to 4, wherein the cooling of the drawn filament is effected by passing the drawn filament through a cooling system having a temperature which is at least 20°C below the temperature at which the filament is drawn.

6. A method according to any of claims 1 to 5, wherein the tensile stress used for drawing is from 5 to 500 kg/cm^2.

7. A method according to claim 6, wherein the tensile stress used for drawing is from 50 to 200 kg/cm^2.

8. A method according to any of claims 1 to 7, wherein the drawn filament is subjected to further drawing.

9. A method for the production of a drawn polymer filament, substantially as hereinbefore described with reference to Figures 1 and 2 of the accompanying drawing.

10. A method for the production of a drawn polymer filament, substantially as described in any of the foregoing Examples.

11. A drawn polymer filament whenever produced by a method according to any of claims 1 to 10.

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1592936 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

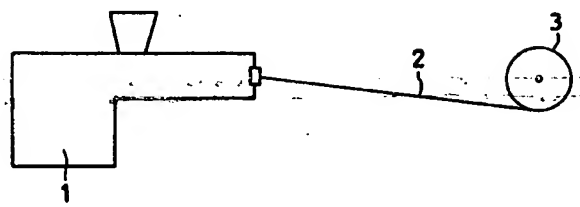

Fig.1

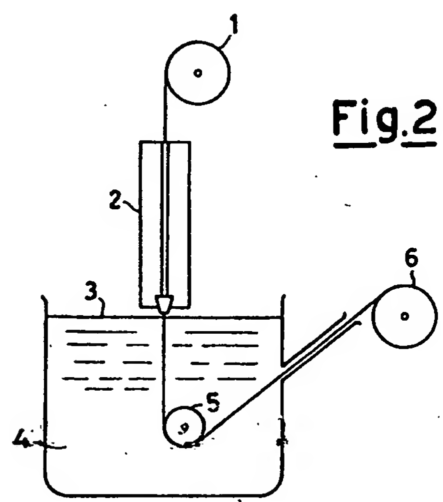

Fig.2